

EXHIBIT 92

Sublimation of Ammonium Salts: A Mechanism Revealed by a First-Principles Study of the NH_4Cl System

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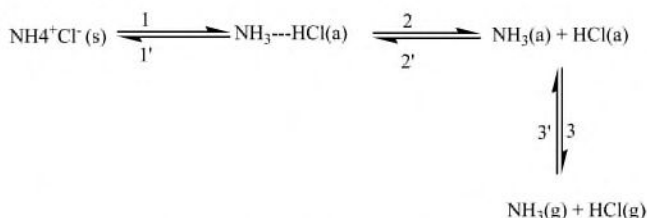
Received: May 6, 2007; In Final Form: July 17, 2007

The mechanism for the sublimation of ammonium salts in general is not well-elucidated; the relationship between sublimation energies and activation energies of sublimation has not been understood. We have studied the kinetics and mechanism for the sublimation of NH_4Cl , a prototype ammonium salt, by first-principles calculations using generalized gradient approximation in the plane-wave density functional theory. Supercells containing 8 to 64 NH_4Cl units were used, and the predicted sublimation energy, 41.0 kcal/mol for $\text{NH}_4\text{Cl}(\text{s}) \rightarrow \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$, is in excellent agreement with the experimental value, 42.2 kcal/mol. The result of statistical-theory calculations indicates that the desorption of the $\text{H}_3\text{N}\cdots\text{HCl}$ molecular complex with a 15.5 ± 1.0 kcal/mol variational barrier, instead of the individual NH_3 and HCl molecules, from the relaxed crystal surface is the rate-controlling step. The desorption rate is predicted to be $25.0 \exp(-13.2 \text{ kcal/mol}/RT)$ cm/s, which is in close agreement with the experimental data. This is the first time the sublimation of an ammonium salt has been successfully modeled quantum mechanically. The result supports the heretofore unexplained experimental finding that the activation energy for the sublimation process is significantly lower than the enthalpic change and that the molecular complex of NH_3 and HCl desorbs concurrently as a pair. In addition, the desorption energies of HCl , NH_3 , and $\text{H}_3\text{N}\cdots\text{HCl}$ from the neat and relaxed NH_4Cl surfaces have been predicted.

1. Introduction

The mechanism for the sublimation of ammonium salts in general is not well-understood. In this study, we attempt to elucidate the detailed mechanism as well as to predict quantitative kinetics for the sublimation process using NH_4Cl as an example. Ammonium chloride (NH_4Cl) is an important industrial compound. X-ray studies of NH_4Cl at room temperature have shown its structure to be of the CsCl type with a unit cell length of 3.866 Å.¹ Neutron diffraction study indicates that at room temperature the structure involves a disorder in the orientation of ammonium ions, the N–H distance was determined to be 1.03 ± 0.02 Å.² It exhibits interesting sublimation/decomposition phenomena and the mechanism is not clear. Experimentally, Spingler,³ Schultz and Dekker,⁴ and Chaiken et al.⁵ have investigated the sublimation kinetics of this system. The mechanism was depicted by Knacke et al.⁶ as Scheme 1 where (s) denotes solid, (a) denotes adsorbed species, and (g) denotes gas-phase species. The above mechanism implies that the sublimation of $\text{NH}_4\text{Cl}(\text{s})$ occurs by the separate and independent desorption of NH_3 and HCl . Experimentally, the activation energy for the sublimation process was reported to be 13.5 ± 2.0 kcal/mol,^{3–5} which is significantly lower than the endothermicity (42.2 kcal/mol)⁷ of the process. On the basis of the relatively small 13.5 kcal/mol activation energy, Knacke et al.⁶ considered reaction step 1 to be rate-controlling, whereas the results of a hot-plate linear pyrolysis experiment by Schultz and Dekker⁴ suggested that desorption step 3 was the rate-determining step. Theoretically, Schultz and Dekker⁸ interpreted the decomposition rate on the basis of a modified Langmuir–Hinshelwood bimolecular surface reaction mechanism, giving the desorption rate $B \sim 3.5 \times 10^2 \exp(-11.3 \text{ kcal/mol}/RT)$ cm/sec. In their calculation, the separate desorption of NH_3 and HCl from the surface was assumed to be the rate-controlling

SCHEME 1



step. The activation energy E_a for the linear vaporization of solid NH_4Cl was assumed to be the sum of heats of adsorption of HCl and NH_3 vapors on their crystal surfaces.⁹ It should be pointed out that the crystal surfaces of HCl and NH_3 are characteristically nonionic. No information from a first-principles calculation is available.

In the present work, the (100) surface of the CsCl structure of NH_4Cl was considered throughout. We have carried out the first quantum-chemical calculation in an attempt to elucidate the mechanism of the sublimation process based on the predicted energetics for the different physical and chemical transformations involved. The predicted results will be compared with existing experimental data.

2. Computational Methods

The calculation was carried out with the Vienna ab initio simulation package (VASP)^{10–13} which evaluates the total energy of periodically repeating geometries on the basis of density function theory (DFT) with the pseudopotential approximation. For the periodic boundary condition, the valence electrons were expanded over a plane-wave basis set. The core electron calculations are applied with the cost-effective pseudopotentials implemented in VASP. The expansion includes all plane waves with their kinetic energies smaller than the chosen cutoff energy, that is, $\hbar^2 k^2/2m < E_{\text{cut}}$, where k is the wave vector,

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TABLE 1: Comparison of the Experimental and Calculated Structural Parameters for NH₄Cl in Crystal Environment Calculated by VASP (Distances in Ångströms and Angles in Degrees)

parameter	calculated	expt
lattice constant	4.027 ^a , (4.000) ^b , [3.975] ^c	3.866 ^d
$r_{\text{Cl-H}}$	2.122 ~ 2.133, (2.134 ~ 2.142), [2.123]	
$r_{\text{Cl-N}}$	3.124 ~ 3.135, (3.137 ~ 3.143), [3.124]	
$r_{\text{N-H}}$	1.025 ~ 1.050, (1.023 ~ 1.050), [1.024 ~ 1.050]	1.03 ± 0.02 ^e

^a $2 \times 2 \times 2$ case (8 NH₄Cl) ^b Values in the parentheses are calculated by $3 \times 3 \times 3$ (27 NH₄Cl) case. ^c Values in the square brackets are calculated by $4 \times 4 \times 4$ (64 NH₄Cl) case. ^d Reference 1. ^e Reference 2.

m is the electronic mass, and E_{cut} is the chosen cutoff energy. In this study, cutoff energies of 400 and 550 eV were chosen for structural parameters and single point energy calculations, respectively.

Generalized gradient approximation (GGA)^{14,15} with PW91 exchange-correlation functional¹⁴ was used for the present calculation. The Brillouin-zone (BZ) integration is sampled with $0.05 \times 2\pi$ (1/Å) spacing in reciprocal space by the Monkhorst–Pack scheme.¹⁶ The Fermi-smearing with $\sigma = 0.2$ eV was used. For comparison, different supercells were used in the calculation for elucidation of some characteristics of the system. For the bulk calculation, 8, 27, and 64 NH₄Cl supercells with dimension of $2a \times 2a \times 2a$, $3a \times 3a \times 3a$, and $4a \times 4a \times 4a$ (where a is the lattice constant), along (100), (010), and (001) directions with $3 \times 3 \times 3$, $2 \times 2 \times 2$, and $1 \times 1 \times 1$ Monkhorst–Pack k points, respectively, were employed.

For the calculations of the surface (100), the reconstruction energies, and the decomposition on the surface, the $2 \times 2 \times 2$ model (including 8 NH₄Cl units) was used; the surface is modeled by repeated supercells in three directions: repetition of the in-plane supercells creates an infinite slab, while the periodicity in the direction perpendicular to the slab creates an infinite stack of slabs. To minimize the interaction between the distinct slab surfaces in this infinitely periodic model system, a vacuum region of 36 Å was used to separate the top and bottom surfaces of the slabs; $1 \times 5 \times 5$ Monkhorst–Pack k points (13 irreducible k points) were used in the surface calculation. The dipole corrections were not included in this calculation. On the basis of the optimized crystal structure, the tetrahedron method with Blöchl corrections and the cutoff energy of 550 eV were used to refine the single point energy.

3. Results and Discussion

3.1. Computational Condition Tests. To select a computationally practical and reasonable model, supercells of $2 \times 2 \times 2$ with 8 NH₄Cl units, $3 \times 3 \times 3$ with 27 NH₄Cl units, and $4 \times 4 \times 4$ with 64 NH₄Cl units were employed for the bulk calculations which were performed without any symmetry constraints, and all atomic positions of the molecules were relaxed. The calculated lattice constants are 4.027, 4.000, and 3.975 Å, respectively, from these models as displayed in Table 1. The results show that the lattice constant differences among the 3 models are only about 1%. The values predicted in this work are slightly larger than the experimental value of 3.866 Å.¹ The geometry parameters of NH₄Cl in the crystal environment are also displayed in Table 1. The four N–H bonds in the NH₄ group are not equivalent; the N–H bond pointing to the Cl atom (as shown in Figure 1) is about 0.02 Å longer than the other three. The Cl–H, Cl–N, and N–H bond lengths

obtained from the two larger supercells are close to those calculated by the $2 \times 2 \times 2$ model as shown in Table 1. Experimentally, only the N–H bond length, 1.03 ± 0.02 Å, is available.² The predicted values in this work are in good agreement with this experimental result.

To further ensure the reliability of the computational results, the structures and frequencies of the isolated gas-phase molecules, NH₃, HCl, and the H₃N...HCl complex, which may be the main products on the surface, have been examined by putting isolated HCl, NH₃, and H₃N...HCl molecules in a $15 \times 15 \times 15$ Å³ cubic box with the VASP code and at the B3LYP/6-311+G(3df,2p) level with Gaussian 03.¹⁷ Table 2 displays the calculated and experimental structures of the above molecules. Results of HCl and NH₃ show that the predicted H–Cl and N–H bond lengths agree well with the experimental values,¹⁸ and the differences of these bond lengths calculated by VASP and Gaussian 03 are only 0.005 and 0.004 Å, respectively. Bond angle $\angle \text{HNN}$ in NH₃ is calculated to be 0.1° less than that of the experimental value.¹⁸ For the H₃N...HCl complex, the differences between VASP and Gaussian 03 are 0.05 and 0.11 Å for H–Cl and N–Cl bond lengths, respectively. If the basis set superposition error (BSSE) corrections^{19,20} are included in the B3LYP calculation, the H–Cl bond length is not changed, and the N–Cl bond is only 0.01 Å longer than that obtained without BSSE corrections.

A frequency scaling factor of 0.9614 at the B3LYP/6-311+G-(3df, 2p) level was established²¹ and recommended by NIST.²² The factors at the B3PW91/6-31+G**, B3PW91/6-311G*, and B3PW91/6-311+G(3df,2p) levels^{21,22} are 0.9601, 0.9627, and 0.9573, respectively. Therefore, a scaling factor of 0.96 was used for frequency calculations in both methods, as summarized in Table 3. For HCl and NH₃ molecules, except NH₃ symmetric bending mode (ν_6) which has around 7% difference (72 cm⁻¹) obtained by the two methods, the deviations between these methods are less than 3% for the other modes. The corresponding errors between the calculated and the experimental values^{23–25} are less than 4%. For H₃N...HCl, the experimental data²³ shows that the HCl stretching frequency in the complex decreases by more than 1500 cm⁻¹, comparing with that in the isolated HCl molecule.²³ For this and the other vibrational modes of the complex, the experimental values in matrices could not be reproduced by VASP and Gaussian 03 calculations in this work, neither by MP2²⁶ nor CI²⁷ calculations. The shifts may be ascribed to the matrix and environment effects.²⁸ The frequencies for NH₄Cl in the crystal environment were calculated by using the $2 \times 2 \times 2$ model; predicted values are in good agreement with experimental data²⁹ as shown in Table 3.

3.2. Sublimation Energy. The sublimation energy of the NH₄Cl crystal was calculated as the energy difference between a single fully optimized NH₄Cl molecule in the crystal and that of the gas-phase products, NH₃ + HCl; that is,

$$\Delta H_{\text{sub}} = E[\text{NH}_3(\text{g}) + \text{HCl}(\text{g})] - [E(\text{supercell})]/X$$

where, X is the number of NH₄Cl units in the supercell. For the $X = 8$ case, the calculated value, $\Delta H_{\text{sub}} = 41.0$ kcal/mol, is close to the experimental value, 42.2 kcal/mol.⁷

The good reproducibility of the experimental values for the sublimation energy, the structures, and the frequencies as discussed above indicates that the $2 \times 2 \times 2$ model is good enough to represent the NH₄Cl crystal.

3.3. Surface and Reconstruction Energies. When a surface is created by cleaving from the bulk material, there will be a rearrangement of atoms near the surface. In order to get an accurate surface energy, one must take into account the surface

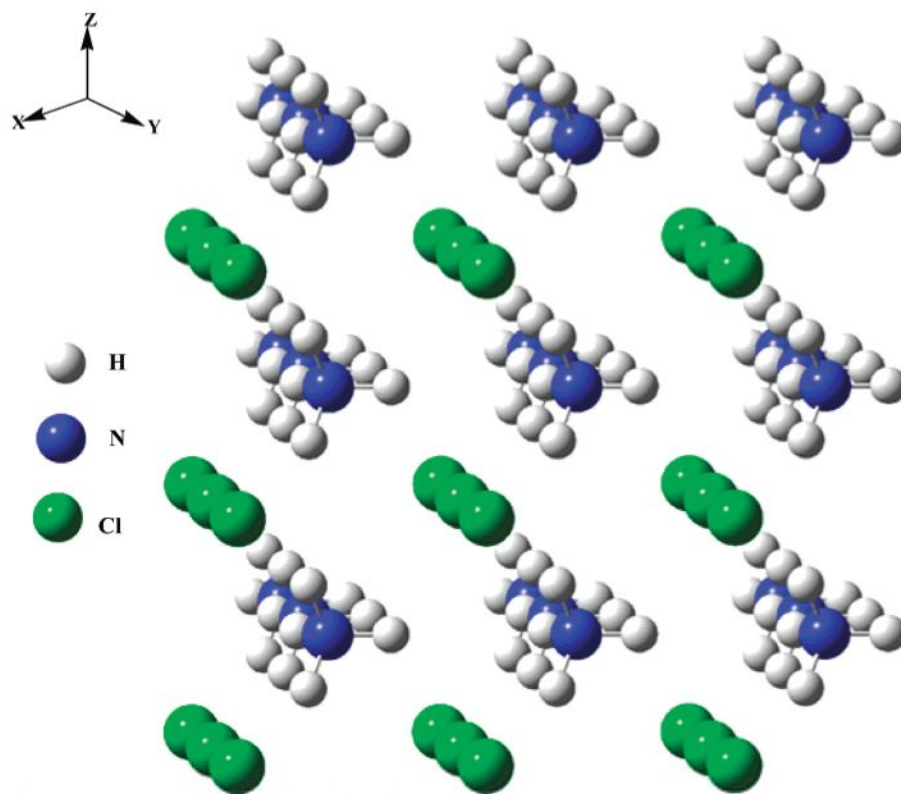


Figure 1. Optimized geometry for the $3 \times 3 \times 3$ NH_4Cl crystal model.

TABLE 2: Structural Parameters for NH_3 , HCl , and $\text{H}_3\text{N}\cdots\text{HCl}$ Complex in the Gas Phase Calculated by VASP and at the B3LYP/6-311+G(3df, 2p) Level by Gaussian 03 (Distances in Ångstrom and Angles in Degrees)

parameter	VASP	B3LYP	expt
HCl			
$R_{\text{H-Cl}}$	1.285	1.280	1.284 ^a
NH_3			
$R_{\text{N-H}}$	1.018	1.014	1.016 ^a
$\angle \text{H-N-H}$	107.3	107.2	107.3 ^a
$\text{H}_3\text{N}\cdots\text{HCl}$			
$R_{\text{H-Cl}}$	1.389	1.339	
$R_{\text{N-Cl}}$	2.971	3.081	3.136 ^a
$\angle \text{HNH}$	108.6	108.0	

^a Reference 18.

relaxation by allowing the surface atoms to reach their minimum energy positions. To prevent the interaction of the desorbed species with the upper surface, the two slabs were separated by 36.0 Å in this work. The surface energy was then calculated according to the following formula:³⁰

$$E_{\text{surf}}^{\text{relax}} = \frac{1}{2S} (E_{\text{slab}} - E_{\text{bulk}}) \quad (2)$$

where S is the surface area of the slab, E_{slab} is the total energy of the slab with relaxation for all surface atoms, and E_{bulk} is the energy of the bulk containing the same number of NH_4Cl units. The factor of 2 used in eq 2 is because of the two surfaces containing the vacuum space. The predicted value $E_{\text{surf}}^{\text{relax}}$ in this work is 101.5 mV/Å². If E_{slab} is taken as the total energy of the unrelaxed slab, that is, the atomic positions in the slab are fixed, the surface energy for the unrelaxed surface is predicted to be $E_{\text{surf}}^{\text{unrelax}} = 301.2$ mV/Å². The energy difference of $E_{\text{surf}}^{\text{unrelax}} - E_{\text{surf}}^{\text{relax}}$ was defined as the surface relaxation energy.³⁰ The predicted reconstruction or relaxation energy is 199.7 mV/Å²,

which is 18.7 kcal/mol per NH_4Cl unit. If a bigger $3 \times 3 \times 3$ model was used, the predicted relaxation energy is 17.2 kcal/mol per NH_4Cl unit, which is reasonably close to that obtained with the $2 \times 2 \times 2$ model.

3.4. Desorption Energies of HCl , NH_3 , and $\text{H}_3\text{N}\cdots\text{HCl}$ from a Clean NH_4Cl Surface. The desorption energies of $\text{H}_3\text{N}\cdots\text{HCl}$, NH_3 , and HCl individually adsorbed on a neat crystal surface of NH_4Cl have been computed. Their adsorption configurations are presented in Figure 2a–c. The desorption energy (E_{des}) was calculated according to the expression

$$E_{\text{des}} = E_{\text{molec}} + E_{\text{slab}} - E_{(\text{molec}+\text{slab})}$$

where E_{molec} is the energy of the gas-phase molecule for $\text{H}_3\text{N}\cdots\text{HCl}$, NH_3 , or HCl in their equilibrium position, E_{slab} is the total energy of the slab with the 36 Å vacuum space, and $E_{(\text{molec}+\text{slab})}$ is the total energy of the adsorbate/slab system. The same conditions have been used to calculate the energies of the bare slab and of the slab–molecule system. For the HCl adsorbed on the surface (see Figure 2a), the molecule is oriented almost perpendicularly to the surface with the Cl atom pointing downward to one of the H atoms in an NH_4 group on the surface with a 2.544 Å Cl \cdots H distance. The predicted E_{des} is 2.6 kcal/mol. For NH_3 adsorption as shown in Figure 2b, the N atom of NH_3 points to one of the H atoms on the surface to form an N \cdots H hydrogen bond with 1.802 Å separation, and the predicted E_{des} is 4.9 kcal/mol. Apparently, the sum of the heats of physical adsorption for HCl and NH_3 vapors on the NH_4Cl crystal surface ($2.6 + 4.9 = 7.5$ kcal/mol) is less than the activation energy 11.3 kcal/mol estimated by Schultz and Dekker.⁸ In the equilibrium configuration of $\text{H}_3\text{N}\cdots\text{HCl}$ adsorbed on the surface as shown in Figure 2c, the Cl atom of the complex connects to one of the H atoms on the surface with a Cl \cdots H hydrogen bond of 2.090 Å; the N–H and the H–Cl bond lengths in the $\text{H}_3\text{N}\cdots\text{HCl}$ pair are 1.216 and 1.583 Å, respectively, which are 0.366 Å shorter and 0.194 Å longer than those in the isolated

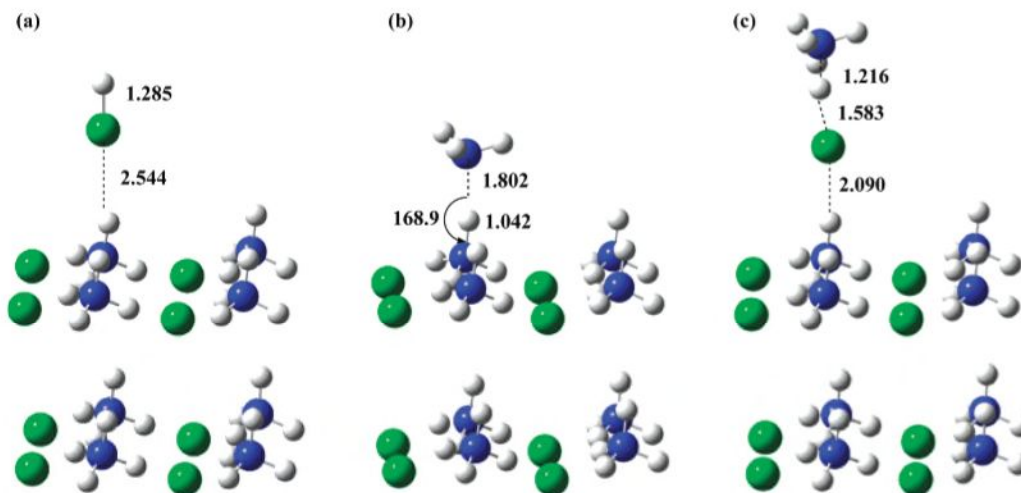


Figure 2. Equilibrium configuration for HCl, NH₃, and H₃N...HCl adsorbed on the pure NH₄Cl surface.

TABLE 3: Comparison of the Experimental and Calculated Vibrational Frequencies Scaled by 0.96¹⁹ by VASP (PW91 in a Plane Wave Basis) and at the B3LYP/6-311+G(3df, 2p) Level for HCl, NH₃, and H₃N...HCl Complex in Gas Phase and NH₄Cl in Crystal

HCl(g)					NH ₃ (g)				
mode	assignment ^a	VASP	B3LYP	expt	mode	assignment ^a	VASP	B3LYP	expt
ν_1	HCl s	2789	2835	2888 ^b	ν_1	NH ₃ asym s	3447	3451	3435, ^b 3447 ^c
					ν_2	NH ₃ asym s	3447	3451	3435, ^b 3447 ^c
					ν_3	NH ₃ sym s	3311	3339	3337, ^d 3345 ^c
					ν_4	NH ₃ asym b	1548	1598	1627, ^d 1639 ^{b,c}
					ν_5	NH ₃ asym b	1548	1598	1627, ^d 1639 ^{b,c}
					ν_6	NH ₃ sym b	916	988	950, ^d 974 ^{b,c}

H ₃ N...HCl complex (g)					NH ₄ Cl(s)			
mode	assignment ^a	VASP	B3LYP	expt ^b	mode	assignment	VASP	expt ^c
ν_1	NH ₃ asym s	3455	3456	3420	ν_1	NH ₄ asym s	3375	3200
ν_2	NH ₃ asym s	3454	3455	3420	ν_2	NH ₄ asym s	3223	3138
ν_3	NH ₃ sym s	3327	3341		ν_3	NH ₄ asym s	2928	3044
ν_4	HCl s	1918	2093	1371	ν_4	NH ₄ asym s	2865	2810
ν_5	NH ₃ asym b	1637	1594		ν_5	NH ₄ asym b	1575	1682
ν_6	NH ₃ asym b	1636	1593		ν_6	NH ₄ asym b	1543	1445
ν_7	NH ₃ sym b	1126	1057	1072	ν_7	NH ₃ sym b	1404	1403
ν_8	HCl b, NH ₃ wag	857	784	1289	ν_8	NH ₄ asym b	1354	
ν_9	HCl b, NH ₃ wag	856	784	1289	ν_9	NH ₄ asym b	1248	
ν_{10}	HCl b, NH ₃ rock	279	238	733	ν_{10}	NH ₄ rock	293	359 (262)
ν_{11}	HCl b, NH ₃ rock	276	237	733	ν_{11}	NH ₄ rock	244	
ν_{12}	H ₃ N-HCl s	203	179	166	ν_{12}	NH ₄ rot	176	168

^a s = stretching, b = bending, wag = wagging, rock = rocking, sym = symmetric, asym = asymmetric, rot = rotation. ^b Reference 23. ^c Reference 24. ^d Reference 25. ^e Reference 29.

gas-phase H₃N...HCl complex, respectively. E_{des} was predicted to be 6.1 kcal/mol. These values, particularly the 7.5 kcal/mol energy sum of HCl and NH₃, are much lower than the experimental sublimation activation energy,³⁻⁵ 13.5 ± 2.0 kcal/mol, indicating that the desorption of HCl and NH₃ from the neat surface cannot represent the sublimation process; in fact, the adsorbed HCl, NH₃, and H₃N...HCl complex may not exist on the neat NH₄Cl surface in view of their low adsorption energies. This result is inconsistent with the mechanism suggested by Schultz and Dekker⁸ and depicted by Knacke⁶ as shown in Scheme 1.

3.5. Desorption Energies of HCl, NH₃, and H₃N...HCl from a Relaxed Top Layer. The desorption energy E_{des} for HCl, NH₃, and one of the NH₄⁺Cl⁻ molecules desorbing from the relaxed surface is defined as

$$E_{\text{des}} = [E_{\text{slab}}(\text{hole}) + E_{\text{molec}}(\text{g})] - E_{\text{slab}}$$

where $E_{\text{slab}}(\text{hole})$ is the energy of the slab after eliminating a molecule (HCl, NH₃, or H₃N...HCl); E_{molec} is the energy of the isolated HCl, NH₃, and H₃N...HCl in the gas phase; and E_{slab} is the total energy of the slab with the 36 Å vacuum space. $E_{\text{molec}}(\text{g})$ was calculated in a $15 \times 15 \times 15$ Å³ cubic box. E_{des} was predicted to be 20.1, 27.0, and 15.5 kcal/mol for HCl, NH₃, and H₃N...HCl desorbing from the top relaxed layer, respectively. These values are much larger than those for the desorption of the same species from a neat NH₄Cl crystalline surface. Significantly, the desorption of HCl and NH₃ individually from the relaxed first surface layer cannot compete with that of H₃N...HCl as a pair. These data indicate that the molecular complex of NH₃ and HCl desorbs concurrently as a pair instead of the separated NH₃ and HCl molecules. To confirm the desorption energy of the H₃N...HCl pair from the relaxed surface, the $3 \times 3 \times 3$ model was also used, and the predicted value, 16.5 kcal/mol at $R = \infty$, is in close agreement with 15.5

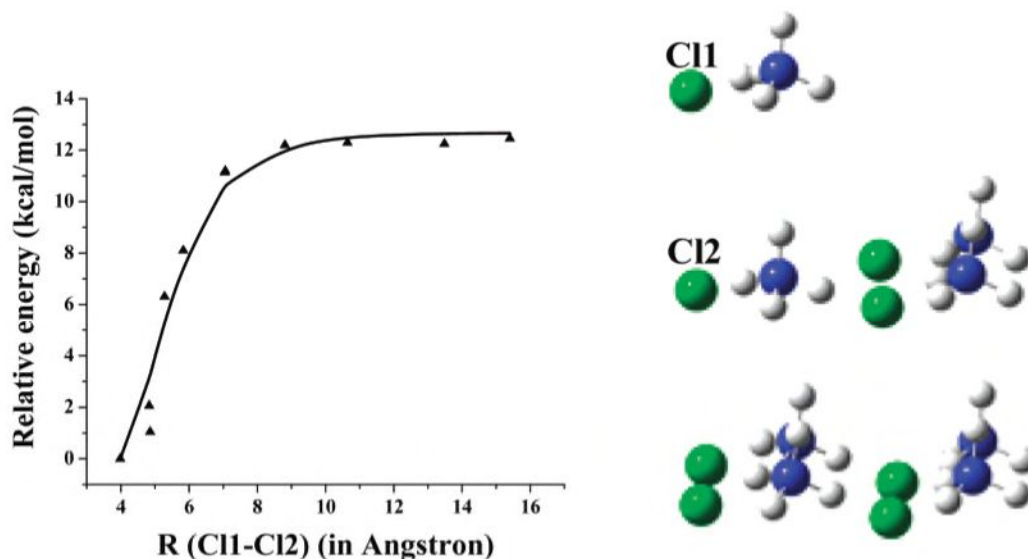


Figure 3. Relative energy for one NH_4Cl molecule dissociated from the relaxed crystal environment, where R represents the distance between Cl1 and Cl2 as the configuration indicated in the figure; triangle symbol is the calculated value; solid line is the fitted curve using Morse function.

kcal/mol obtained by the $2 \times 2 \times 2$ model. The desorption-adsorption energy for the $\text{NH}_3\text{--HCl}$ pair predicted in this work, 15.5 kcal/mol is also in close agreement with 13.5 ± 2.0 kcal/mol of the experimental activation energy for sublimation. Schultz and Dekker⁸ and Hill³¹ estimated the desorption activation energy of $\text{NH}_3\text{--HCl}$ to be $10.4 \pm (0.6\sim 2.0)$ and 11.3 kcal/mol, respectively, by assuming that the activation energy could be approximated by the sum of the heats of physical adsorption of HCl and NH_3 on the NH_4Cl surface. These values are noticeably lower than the 15.5 kcal/mol energy predicted by the $2 \times 2 \times 2$ supercell model calculation.

The desorbed $\text{H}_3\text{N}\cdots\text{HCl}(\text{g})$ complex dissociates rapidly to $\text{NH}_3(\text{g})$ and $\text{HCl}(\text{g})$ without a distinct transition state as one would expect. The calculated dissociation energy (D_e) for this process by VASP is 11.2 kcal/mol. Experimentally, Goldfinger and Verhaegen³² reported a D_0 value of 10.0 ± 3.0 kcal/mol, or $D_e = 12.3 \pm 3.0$ kcal/mol if the zero-point energy calculated at the B3LYP/6-311+G(3df, 2p) level was included. With a higher level calculation by CCSD(T)/6-311+G(3df,2p)/B3LYP/6-311+G(3df,2p) using the Gaussian 03 code, D_e for the $\text{H}_3\text{N}\cdots\text{HCl}$ complex is 8.0 kcal/mol. This value should be more reliable.

From the above discussion, we see that one of the NH_4^+Cl^- molecules desorbing from the relaxed surface is the major step of the sublimation process. In order to investigate this process, the $2 \times 2 \times 2$ model was used. The plane consisting of Cl atoms on the first layer was defined as the reference surface, one of the top layer NH_4Cl molecules was pulled off along the Z axis from the relaxed surface, the distance between the Cl atom (Cl1) in the dissociated NH_4Cl and another Cl atom (Cl2) in one of the neighboring NH_4Cl lying in the reference surface is defined as R as shown in Figure 3. The structure of each point was fully optimized without any constraint. No distinct intrinsic transition state was found in the calculation. The dissociation energy (triangle symbol) with the separation (R) is plotted in Figure 3. The selected structures for the relaxed surface and the dissociated product with $R = 15.4$ Å are shown in Figure 4a,b. The result indicates that the proton gradually transfers from NH_4^+ side to Cl^- side as R is increasing. In the $\text{H}_3\text{N}\cdots\text{HCl}$ pair at $R = 15.4$ Å (see Figure 4), the N–H and H–Cl bond lengths and Cl–H–N bond angle are 1.375, 1.492 Å and 178.2° , respectively; the other three N–H bonds are 1.025, 1.019, and 1.018 Å. In the gas phase of $\text{H}_3\text{N}\cdots\text{HCl}$, the

corresponding values are 1.582 and 1.389 Å, and 180.0° for N–H and H–Cl bond lengths and Cl–H–N bond angle; the other three N–H bonds are equal with a 1.019 Å value. The relative dissociation energy at $R = 15.4$ Å is 12.4 kcal/mol, which is 3.1 kcal/mol lower than the value (15.5 kcal/mol) at $R = \infty$. To investigate the possible factors producing this difference, the vacuum space of 46 Å and $R = 15.0$ and 20 Å were used; D_e for both cases is 12.3 kcal/mol which is also close to 12.4 kcal/mol under the conditions of 36 Å vacuum space and $R = 15.4$ Å. These values indicate that, with the vacuum space of 36 or 46 Å, the dissociation process already reaches its limit. The dissociation energy deviation may arise from the structural differences of $\text{H}_3\text{N}\cdots\text{HCl}$ calculated in the slab and in its gas phase as shown above. In the slab calculation, 36 or 46 Å vacuum space is added to the Z axis, which is enough for the $\text{H}_3\text{N}\cdots\text{HCl}$ gas-phase calculation in this direction. However, in the X and Y directions, the lattice constant values are kept the same as those in the bulk (8.06 Å); they are not enough for the gas-phase calculation in these two directions. Therefore, the $\text{H}_3\text{N}\cdots\text{HCl}$ pair in the slab at $R = 15$ or 20 Å does not reach the real gas-phase ($R = \infty$ for 3 dimensions) because of the slab limitation, which results in the 3.1 kcal/mol difference as mentioned above. We also tested the dissociation barrier of $\text{H}_3\text{N}\cdots\text{HCl}$ from (010) and (001) surfaces at $R = \infty$; the results show that $\text{H}_3\text{N}\cdots\text{HCl}$ which decomposes from the (001) surface needs a 17.3 kcal/mol barrier, which is 1.9 kcal/mol larger than that from the (100) surface. However, on the (010) surface, we suffered from a convergence problem and did not obtain a definite value.

3.6. Proposed Sublimation/Dissociation Mechanism. On the basis of the above discussion, we suggest that the sublimation/dissociation reaction is a multistage process, which takes place as shown in Scheme 2. In Scheme 2, c refers to NH_4^+Cl^- in the crystal environment (bulk), s refers to the relaxed surface, and g refers to the gas phase. The energy diagram for this process is plotted in Figure 5 in which step 1 involves the surface reconstruction with energy of 18.7 ± 1.0 kcal/mol per NH_4Cl unit as cited above; in step 2, one of the NH_4Cl molecules undergoes proton transfer from NH_4^+ to Cl^- and desorbs from the relaxed surface as a pair, $\text{H}_3\text{N}\cdots\text{HCl}(\text{g})$, with a 15.5 kcal/mol barrier with approximately ± 1 kcal/mol energy deviation from the use of different supercell sizes. In step 3, $\text{H}_3\text{N}\cdots\text{HCl}(\text{g})$ dissociates rapidly to $\text{NH}_3(\text{g}) + \text{HCl}(\text{g})$ because of the weak

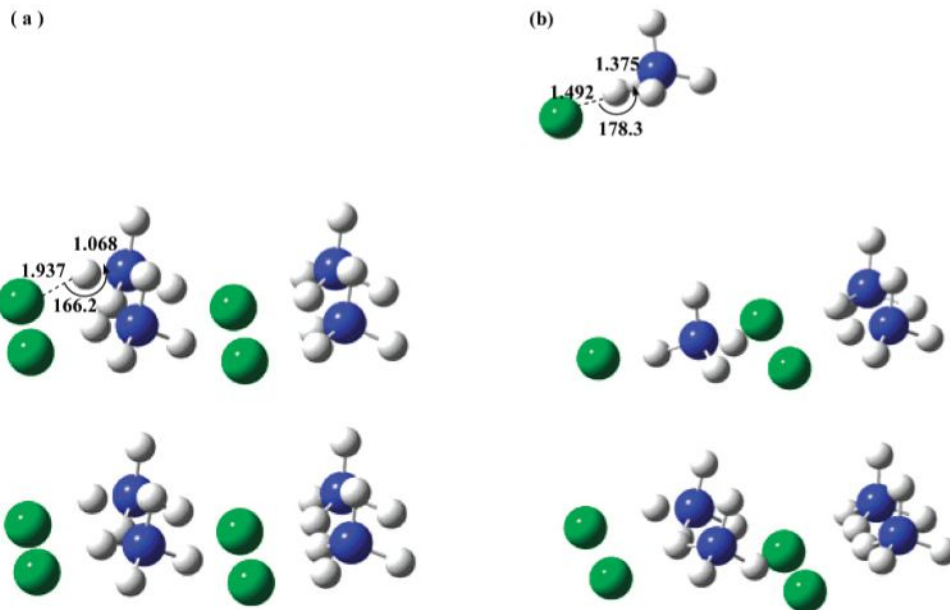


Figure 4. Optimized configurations for (a) the relaxed crystal surface and (b) one of the dissociation products with $R = 15.4 \text{ \AA}$.

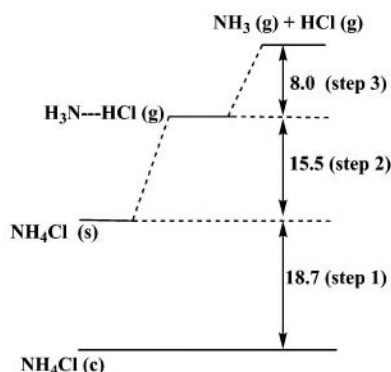
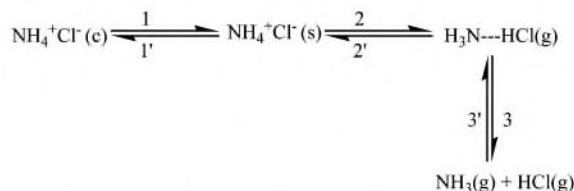


Figure 5. Schematic energy diagram (in kilocalorie per mole) for the sublimation/dissociation processes of NH_4Cl , where $\text{NH}_4\text{Cl}(\text{c})$ refers to NH_4Cl in the crystal environment; $\text{NH}_4\text{Cl}(\text{s})$ represents NH_4Cl on the relaxation surface; and $\text{H}_3\text{N}\cdots\text{HCl}(\text{g})$ represents the gas-phase $\text{H}_3\text{N}\cdots\text{HCl}$ pair; $[\text{NH}_3(\text{g}) + \text{HCl}(\text{g})]$ represents the products in the gas phase.

SCHEME 2



$\text{N}\cdots\text{H}$ bond (1.582 \AA) in $\text{H}_3\text{N}\cdots\text{HCl}(\text{g})$ and the low dissociation energy (8 kcal/mol predicted by the CCSD(T) calculation with an uncertainty of about $1\text{--}2 \text{ kcal/mol}$). The heat of sublimation estimated from the energies for the 3 steps, 42 kcal/mol with about 10% uncertainty, is in excellent agreement with the 42.2 kcal/mol experimental value as well as with the 41 kcal/mol result predicted for the overall sublimation process, $\text{NH}_4\text{Cl}(\text{c}) \rightarrow \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$ as aforementioned. Apparently, the formation and desorption of the $\text{H}_3\text{N}\cdots\text{HCl}(\text{g})$ pair from the crystal environment (step 2) is the rate-controlling step. The desorption rate for step 2 and the unimolecular dissociation rate for step 3 have been calculated and presented in the following section.

3.7. Prediction of Sublimation Rate. For the sublimation of a solid, the linear rate of regression can be given by the following equation:⁴

$$B = n_s \frac{M}{\rho N} k_s \text{ cm sec}^{-1} \quad (1)$$

in which n_s = number of molecules per cm^2 surface $= (\rho N / M)^{2/3}$; M = molecular weight, g mol^{-1} ; ρ = density of solid, g cm^{-3} ; N = Avogadro number, molecules mol^{-1} ; k_s = molecular desorption rate constant, s^{-1} .

According to the transition state theory,³³

$$k_s = \frac{k_B T}{h} \frac{Q^*}{Q} \exp(-E_0 / k_B T) \quad (2)$$

so that eq 1 becomes

$$B = \left(\frac{M}{\rho N} \right)^{1/3} \frac{k_B T}{h} \frac{Q^*}{Q} \exp(-E_0 / k_B T) \text{ cm/s} \quad (3)$$

Here, k_B is the Boltzmann constant, T is the temperature, h is the Planck's constant, E_0 is the energy of activation per molecule at 0 K , and Q^* and Q are the molecular partition function for the transition state and the reactant, respectively.

The decomposition process, $(\text{NH}_4\text{Cl})_X \rightarrow (\text{NH}_4\text{Cl})_{X-1} + \text{H}_3\text{N}\cdots\text{HCl}(\text{g})$, is a barrierless dissociation reaction as calculated above for $X = 8$. The potential energy along the minimum energy path (MEP) is shown in Figure 3. The necessary information (the structures, frequencies, etc.) to calculate molecular partition functions for the reactant and transition state is provided by VASP calculations. Transition state parameters for the barrierless decomposition processes were evaluated canonically for each temperature and critical separation, $r^*(T)$, on the basis of the maximum Gibbs free energy criterion as described in refs 34 and 35. The result shows that, in the temperature range of $300\text{--}1000 \text{ K}$, the transition state locates at nearly the same configuration. The predicted structures, frequencies, and energies are used in the rate calculations. It should be mentioned that there are several imaginary frequencies corresponding to NH_4^+ rotations in the relaxed surface and the transition state. Fortunately, those imaginary

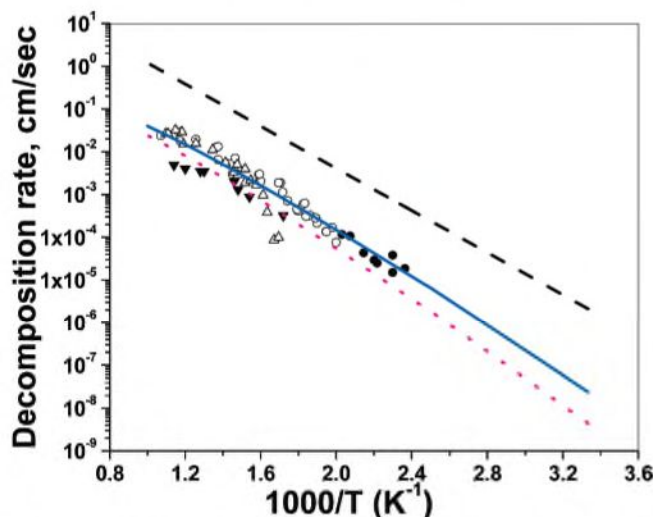


Figure 6. Comparison of the predicted surface regression rates with experimental available values. Symbols are the experimental values: ●, ref 3; ○, ref 5 (at 1–2 mmHg of environmental pressure); △, ref 5 (at 760 mmHg environmental pressure); ▼, ref 4. Dotted and solid lines represent the predicted results in this work using $D_0 = 15.5$ and 14.5 kcal/mol, respectively. Dashed line is the estimated value by Schultz and Dekker⁸ with the apparent activation energy of 11.3 kcal/mol.

frequencies cancel out from each other in the rate constant calculation. As known, in eq 3, $Q = Q_{\text{trans}}Q_{\text{rot}}Q_{\text{vib}}Q_{\text{ele}}$, where Q_{trans} , Q_{rot} , Q_{vib} , and Q_{ele} represent the translation, rotation, vibration, and electronic excitation partition functions, respectively. Among them, only Q_{vib} is related to the molecular frequencies; that is,

$$Q_{\text{vib}} = \prod_i (1 - e^{-h\nu_i/kT})^{-1} \quad (4)$$

From eqs 3 and 4, we see that the contribution from the similar imaginary frequencies in the numerator and denominator can be canceled out from each other. Other partition functions given above are taken to be unity.

The temperature (T) resolved method implemented in the Variflex code³⁶ was used to calculate k_s , and $D_0 = 15.5$ kcal/mol at $R = \infty$ was used in the rate calculation. The predicted values (see Figure 6) are in close agreement with the experimental data of Schultz and Dekker⁴ but are slightly lower than those of Spingler³ and Chaiken et al.⁵ The bulk of experimental data can be accounted for with $D_0 = 15 \pm 1$ kcal/mol. The predicted rate constants, $B = 25.0 \exp(-13.2 \text{ kcal/mol}/RT)$ and $B = 25.0 \exp(-12.2 \text{ kcal/mol}/RT)$ cm/s using $D_0 = 15.5$ and 14.5 kcal/mol, respectively, lie well within the scatter of existing kinetic data. The value estimated by Schultz and Dekker⁸ with 11.3 kcal/mol activation energy using the conventional TST was also shown as the dashed line in Figure 6; the result based on their crude and incorrect model overestimates the sublimation rate.

To confirm that the desorption of NH_4^+Cl^- from the relaxed surface is the rate-controlling step, the dissociation rate of $\text{H}_3\text{N}\cdots\text{HCl}(\text{g}) \rightarrow \text{HCl}(\text{g}) + \text{NH}_3(\text{g})$ was also calculated using the variational RRKM theory.^{37–39} As expected, this process is considerably faster, about 1×10^4 times greater than that of step 2. The rate for this dissociation step can be expressed by $6.92 \times 10^{13} \exp(-7.32 \text{ kcal/mol}/RT) \text{ s}^{-1}$.

4. Conclusion

In this paper, we have performed first-principles calculations using the plane-wave DFT for elucidation of the sublimation/

dissociation mechanism of NH_4Cl . The result of our calculations indicates that three distinct steps are involved in the sublimation. In the first step, NH_4^+Cl^- molecules relax from their crystal structure on the surface after cleaving with about 18.7 ± 1.0 kcal/mol relaxation energy (the same energy accounts for the surface structural relaxation after each layer of NH_4^+Cl^- is desorbed in the sublimation process); in the second step, one of the NH_4^+Cl^- molecules on the surface undergoes proton transfer to form an $\text{HN}_3\cdots\text{HCl}$ complex which desorbs barrierlessly with a 15.5 ± 1.0 kcal/mol energy. In the last step, the molecular complex $\text{HN}_3\cdots\text{HCl}(\text{g})$ dissociates rapidly also without a distinct barrier to $\text{NH}_3(\text{g})$ and $\text{HCl}(\text{g})$ with about 8.0 kcal/mol energy. The dissociation rates for steps 2 and 3 were calculated which indicated that step 2 is the rate-controlling step. The predicted overall sublimation endothermicity, sublimation activation energy, and the sublimation rate are in good agreement with available experimental data, quantitatively explaining for the first time that the activation energy for the sublimation of an ammonium salt is significantly lower than the overall enthalpic change and that the molecular complex of NH_3 and HCl desorbs concurrently as a pair.

Acknowledgment. This work was supported by the Office of Naval Research under Grant N00014-02-1-0133. M.C.L. gratefully acknowledges the supports from Taiwan's MOE ATU program as well as the National Science Council and the Taiwan Semiconductor Manufacturing Co. for the NSC-distinguished visiting professorship and the TSMC distinguished professorship, respectively, at the Center for Interdisciplinary Molecular Science, National Chiao Tung University, Hsinchu, Taiwan. We are very much indebted to Taiwan's National Center for High-Performance Computing for the extensive CPUs needed in this work.

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